

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 709 220 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.05.1996 Bulletin 1996/18

(51) Int Cl.⁶: **B41M 1/36, D21H 19/84**

(21) Application number: **95116881.4**

(22) Date of filing: **26.10.1995**

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **27.10.1994 JP 263721/94**
17.10.1995 JP 268638/95

(71) Applicant: **CANON KABUSHIKI KAISHA**
Tokyo (JP)

(72) Inventors:
• **Hirose, Mifune**
Ohta-ku, Tokyo 146 (JP)

- **Suzuki, Eiichi**
Ohta-ku, Tokyo 146 (JP)
- **Sakaki, Mamoru**
Ohta-ku, Tokyo 146 (JP)
- **Katayama, Masato**
Ohta-ku, Tokyo 146 (JP)

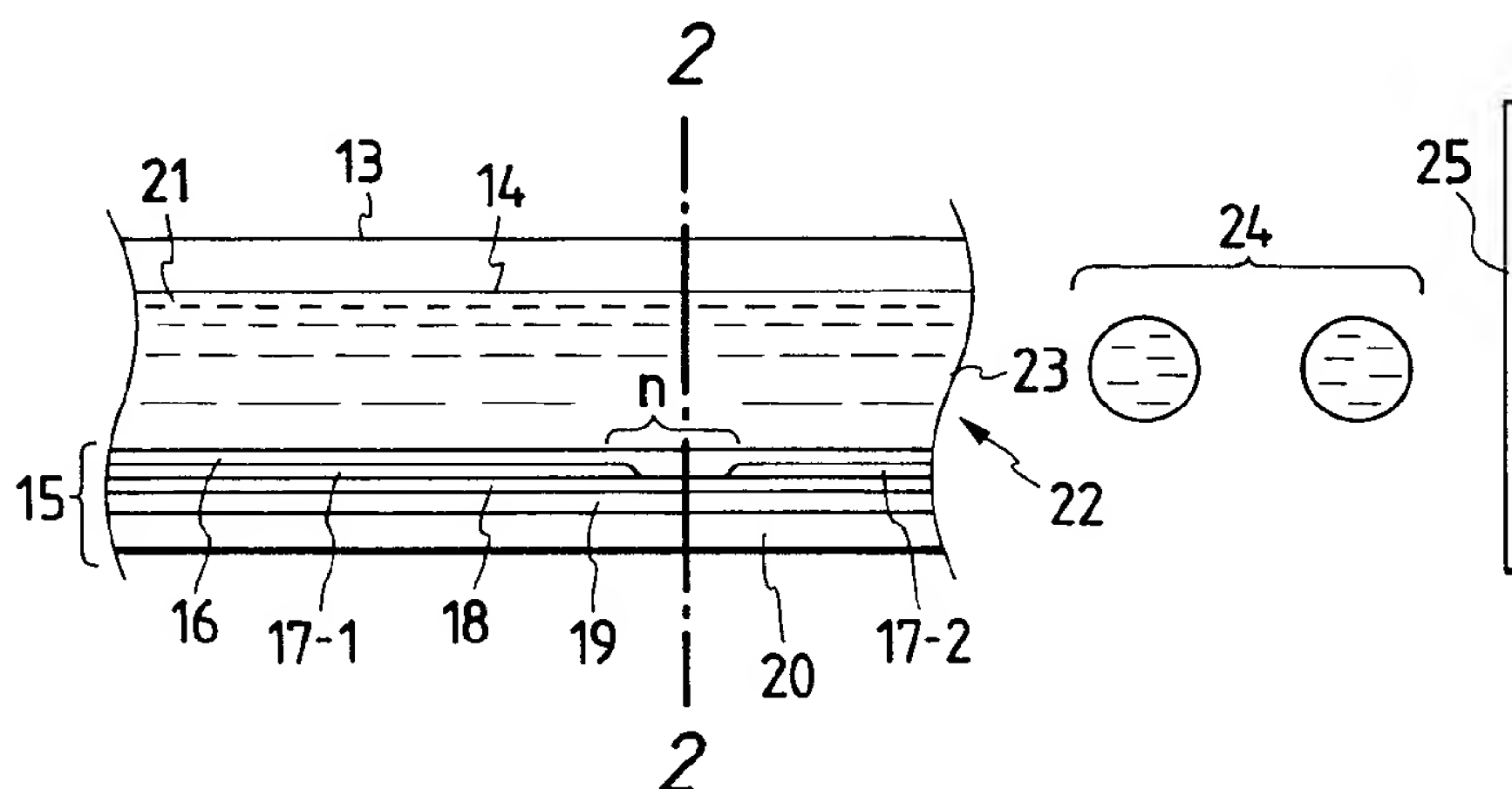
(74) Representative: **Bühling, Gerhard, Dipl.-Chem.**
Patentanwaltsbüro
Tiedtke-Bühling-Kinne & Partner
Bavariaring 4
D-80336 München (DE)

(54) **Recording medium, and image forming method employing the same**

(57) A recording medium is provided which has an ink-receiving layer mainly composed of an inorganic pigment and a binder on one face of an ink-absorbent base

sheet, and a cationic substance applied on, or impregnated into, the reverse face of the base sheet.

FIG. 1



EP 0 709 220 A1

DescriptionBACKGROUND OR THE INVENTION5 Field of the Invention

The present invention relates to a recording medium for color recording, particularly ink-jet color recording, and to an image-forming method employing the recording medium. The present invention also relates to a recording medium suitable for post cards, and other cards.

10 Related Background Art

The ink-jet recording method is attracting attention because of suitability for high speed recording, color printing, and high density recording. Therefore, ink-jet recording apparatuses are widely used. The recording sheets for ink-jet recording are exemplified by those which are disclosed in Japanese Patent Applications Laid-Open Nos. 59-35977, 1-135682 and so forth.

With popularization of color-recording apparatus, post cards and other cards are wanted which are suitable for easy printing of an original color image.

In printing on a post card or a like card, the card as the recording medium is required to have following properties: (1) recording characteristics suitable for ink-jet recording with sharpness and density of image comparable with conventional printing, and preferably surface gloss at least on one face, (2) capability of forming a sharp image by ink-jet recording, and also suitability for writing with a conventional aqueous pen, ball point pen, pencil, or fountain pen, (3) no penetration of ink being caused to the reverse face when an image is recorded on either one face of the recording medium, (4) no feathering being caused even when a drop of water like rain water is brought into contact for hours with the recording medium, and (5) no percolation of re-dissolved recording agent to the reverse face being caused even when a drop of water is brought into contact with the recording medium for hours.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a recording medium useful as post cards and other cards, having the aforementioned required properties.

Another object of the present invention is to provide an image-forming method which enables easy formation of original color images on a post card or other kinds of card at a low cost by ink-jet recording.

According to an aspect of the present invention, there is provided a recording medium having an ink-receiving layer mainly composed of an inorganic pigment and a binder on one face of an ink-absorbent base sheet, and a cationic substance applied or impregnated onto or into the other face of the base sheet.

According to another aspect of the present invention, there is provided an image-forming method comprising applying an ink containing at least a water-soluble dye having an anionic group onto the aforementioned recording medium.

40 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a vertical sectional view of a head portion of an ink-jet recording apparatus employed in the present invention.

Fig. 2 is a lateral sectional view of a head portion of an ink-jet recording apparatus employed in the present invention.

Fig. 3 is a perspective external view of a head portion constructed by multiplication of the heads shown in Figs. 1 and 2.

Fig. 4 is a perspective external view of an ink-jet recording apparatus.

Fig. 5 is a plan view of a post card employing the recording medium of the present invention.

Fig. 6 is a sectional view of the post cards shown in Fig. 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The recording medium of the present invention is composed of a base sheet, an ink-receiving layer formed on one face of the base sheet, and a cationic substance applied onto the other face reverse to the ink-receiving layer.

The ink for the image-forming method of the present invention contains essentially a water-soluble dye having at least an anionic group.

The base sheet employed in the present invention is mainly composed of chemical pulp such as LBKP and NBKP, a size, and a filler, and is formed into a sheet, by using a paper-making auxiliary agent if necessary, in a conventional paper-making process. The pulp employed may additionally contain, or mainly composed of mechanical pulp, or waste paper-regenerated pulp.

5 The size includes rosin sizes, alkylketene dimers, alkenylsuccinic acid anhydrides, petroleum resin type sizes, epichlorohydrin, acrylamide, and the like. The filler includes calcium carbonate, kaolin, talc, titanium dioxide, and the like. Surface sizing treatment may be conducted, if necessary.

The base sheet employed in the present invention is required to have appropriate ink absorbency, having preferably a Stöckigt sizing degree ranging from 0 to 15 seconds. A base sheet of less ink-absorbency requires a larger amount
10 of coating on the both faces thereof in order to obtain sufficient ink absorbency in ink-jet recording. The larger amount of coating would undesirably cause difficulty and high cost in production, low suitability for writing with usual writing tools, low handleableness for use for post cards or other kinds of cards, impairment of recorded image caused by falling-off of the coat layer by folding or surface scratching, generation of paper dust, and so forth.

The basis weight of the base sheet ranges preferably from 100 g/m² to 200 g/m². The basis weight of the recording
15 medium may preferably be in the range of from 120 g/m² to 200 g/m². Since the base sheet itself is ink-absorbent, the recording medium of a basis weight of less than 120 g/m² is liable to cause undesired phenomena such as waving or cockling of the printed portion having received the ink, penetration of ink to the reverse face, namely strike-through, and percolation of re-dissolved recording agent by deposited water drops to the reverse face. The recording medium having a basis weight of more than 200 g/m² is too stiff, tending to exhibit low deliverability in a recording apparatus.

20 The ink-receiving layer formed on the base sheet contains a binder. The binder includes casein, starch; a cellulose derivative such as carboxymethylcellulose, and hydroxymethylcellulose; a hydrophilic resin capable of being swelled by ink such as polyvinyl alcohol, polyvinylpyrrolidone, sodium polyacrylate, and polyacrylamide; a resin having hydrophilic portions and hydrophobic portions in the molecule such as SBR latexes, acrylic emulsions, and styrene-acrylate copolymers.

25 The recording medium of the present invention essentially contains an inorganic pigment in the ink-receiving layer. An organic pigment may be used in combination with the inorganic pigment.

The inorganic pigment includes silica, alumina, aluminum silicate, magnesium silicate, hydrotalcite, calcium carbonate, titanium oxide, clay, talc, and magnesium (basic) carbonate, but is not limited thereto. The organic pigment includes plastic pigments such as urea resins, urea-formalin resins, polyethylene resins, and polystyrene resins, but
30 is not limited thereto.

A water-repellent substance such as silicone oil, paraffin, wax, and fluorine compounds, or the aforementioned size may additionally be used.

The ink-receiving layer may further contain, if necessary, an additive such as a dye-fixing agent, a fluorescent whitener, a surfactant, an antifoaming agent, a pH adjusting agent, an antiseptic agent, a UV absorber, an antioxidant,
35 a dispersant, and a viscosity-reducing agent. Such an additive may be selected from known substances to meet the purpose.

The total amount of the applied pigment in the ink-receiving layer ranges preferably from 0.1 g/m² to 50 g/m², more preferably from 0.1 g/m² to 20 g/m². With a less amount of the pigment, the surface of the base sheet may incompletely be covered. At the amount of pigment of less than 0.1 g/m², the ink-receiving layer is not effective in color development
40 of the dye in comparison with the case of no ink-receiving layer. At the amount of the pigment of more than 50 g/m², the coat layer is liable to cause powder falling-off.

The recording medium of the present invention has essentially a cationic substance applied or impregnated onto or into the face of the base sheet reverse to the ink-receiving layer.

The cationic substance on the reverse face of the base sheet improves the water-fastness and the image density
45 of the recorded image. The cationic substance may be either a low-molecular cationic substance or a high-molecular cationic substance as shown below. Complete water-fastness is obtained by combination of a low-molecular cationic substance having a weight-average molecular weight of not higher than 1000, preferably from 100 to 700, and a high-molecular cationic substance of weight-average molecular weight of not lower than 2000, preferably from 2000 to 10000.

50 In the present invention, when ink is brought into contact with the combination of the low-molecular cationic substance of molecular weight of not higher than 1000 and the high-molecular cationic substance mentioned above on the recording medium or at the site of penetration, the low-molecular cationic substance is re-dissolved in the ink. Thereby, the low-molecular cationic substance will associate with dye in the ink by ionic interaction, and be separated from the solution phase instantaneously as the first step of reaction of the recording medium with the ink.

55 Then, as the second step of the reaction, the association product of the low-molecular cationic substance with the dye is adsorbed by the high-molecular cationic substance of molecular weight of not lower than 2000, resulting in increase in dimension of the dye agglomerate formed by the association. Therefore, the dye does not readily penetrate into interstices between fibers of the recording medium, and only the liquid portion after the solid-liquid separation

penetrates into the recording medium. Thereby, image quality and ink fixability are both improved. Further, since the agglomerate formed from the low-molecular cationic substance, the anionic dye and the high-molecular substance of molecular weight of not lower than 2000 as mentioned above has an extremely high viscosity, the agglomerate will not migrate with the liquid medium. Consequently, color mixing, or bleeding, will not occur between the adjacent dots of different colors in color printing like the aforementioned full color image formation. The agglomerate is inherently water-insoluble, rendering the water-fastness of the formed image perfect.

The low-molecular cationic substance having a molecular weight of not higher than 1000 specifically includes hydrochlorides and acetates of primary, secondary, and tertiary amines such as laurylamine, coconut-amine, stearylamine, and rosin-amine; quaternary ammonium compounds such as lauryltrimethylammonium chloride, lauryldimethylbenzylammonium chloride, benzyltributylammonium chloride, and benzalkonium chloride; pyridinium type compounds such as cetylpyridinium chloride, and cetylpyridinium bromide; imidazoline type cationic compounds such as 2-heptadecenyl-hydroxyethylimidazoline; and ethylene oxide adducts of higher alkylamines such as dihydroxyethyl-stearylamine. Further, in the present invention, an amphoteric surfactant may be used which is cationic in a certain pH region. More specifically, the amphoteric surfactant includes carboxylate salt type amphoteric surfactants such as amino acid type amphoteric surfactants, compounds of $R-NH-CH_2-CH_2-COOH$ type, and betaine type compounds like stearyldimethyl-betaine and lauryldihydroxyethylbetaine; sulfate ester type amphoteric surfactants, sulfonate salt type amphoteric surfactant, and phosphate ester type amphoteric surfactants. Naturally, such a type of amphoteric surfactant should be used with a recording medium having a pH of lower than the isoelectric point thereof or with an ink adjusted to have a pH of lower than the isoelectric point on mixing with the amphoteric surfactant.

A metallic compound may be used therefor, such as aluminum lactate, basic polyaluminum hydroxide, aluminum chloride, sodium aluminate, and aluminum acrylate. Of these metallic compounds, particularly preferred are benzalkonium chloride, benzyltributylammonium chloride, basic aluminum salts, and low-molecular polyallylamines.

The low-molecular cationic compound useful in the present invention is not limited to those mentioned above.

The function and the effect of the high-molecular weight cationic compound of molecular weight of not lower than 2000 in the present invention are described above. That is, in the second step of the reaction of the recording medium with the ink, the association product of the low-molecular cationic substance with the dye is adsorbed by the high-molecular cationic substance of molecular weight of not lower than 2000, resulting in increase in dimension of the dye agglomerate formed by the association. Therefore, the dye cannot readily penetrate into interstices between fibers of the recording medium, and only the liquid portion resulting from the solid-liquid separation penetrates into the recording medium. Thereby, image quality and ink fixability are both improved.

The high-molecular cationic substance, which has a molecular weight of not lower than 2000, is sufficiently effective in practicing the present invention. The molecular weight is preferably in the range of from 2000 to 10000 for obtaining high image density. Without the low-molecular cationic substance of molecular weight of not higher than 1000, the effect of the association is low. Without the high-molecular cationic substance of molecular weight of not lower than 2000, the effect of the agglomeration is insufficient.

As described above, the use of combination of two kinds of cationic substances leads to a higher degrees of water-fastness.

The high-molecular cationic substance having a molecular weight of not lower than 2000 specifically includes polyallylamine and salts thereof, e.g., hydrochloride; polyaminesulfonic acid and salts thereof, e.g., hydrochloride; polyvinylamine and salts thereof, e.g., hydrochloride; chitosan and salts thereof, e.g., acetate, but is not limited thereto. The type of salt thereof is not limited to hydrochloride and acetate.

The high-molecular cationic substance may be prepared by partially cationizing a nonionic high-molecular substance. Specific examples thereof include a copolymer of vinylpyrrolidone and a quaternary salt of an aminomethylalkyl acrylate, a copolymer of acrylamide and a quaternary salt of aminomethylacrylamide, and the like, but are not limited thereto. Of the above compound, particularly preferred are polyallylamine salts, chitosan salts, and cationic acrylamides.

The aforementioned high-molecular substance or the cationic high-molecular substance is preferably water-soluble, but may be dispersible in a state of a latex or an emulsion.

The ratio of the low-molecular cationic substance to the high-molecular cationic substance is preferably in the range of from 20/1 to 1/20 by weight. Within this range, the recorded image has higher water-fastness as well as higher image quality and higher image density.

The cationic components is contained in the recording medium preferably in an amount of from 0.05 g/m² to 7 g/m². At the amount of lower than 0.05 g/m², the effect of the cationic substance is not achieved, whereas at the amount of higher than 7 g/m², the ink absorbency is lower and bleeding is liable to occur. More preferably the applied amount is in the range of from 0.3 to 3 g/m². At the amount of less than 0.3 g/m², the bleeding and the water-fastness are not improved sufficiently, whereas at the amount of more than 3 g/m², the light-fastness and the image density are tends to be lower.

An inorganic pigment or an organic pigment may be used in combination with the cationic substance.

The recording medium of the present invention is prepared from the above materials.

The recording medium may be prepared by firstly applying a cationic substance and then forming an ink-receiving layer on a base sheet, or in another way, by firstly forming an ink-receiving layer on a face of a base sheet and then applying a cationic substance on the other face thereof.

5 The cationic substance may be applied onto a base sheet in a mixture with the aforementioned surface-sizing aqueous coating liquid. Otherwise, the cationic substance contained in a liquid may be applied or impregnated onto or into a base sheet after application and drying of the aqueous coating liquid on a substrate.

In preparation of the ink-receiving layer, an aqueous coating liquid containing a pigment, a binder, and other additives as mentioned above is applied on the surface of a base sheet by a conventional method such as a roll coater method, a blade coater method, an air knife coater method, a gate roll coater method, a size press method, and a shim size method, and subsequently the coated matter is dried by an air drier, a heating drum, or the like. Further the resulting recording medium may be supercalendered for smoothening or strengthening of the surface.

For imparting gloss to the surface of the ink-receiving layer, casting treatment of the outermost layer is preferred to the supercalender treatment.

15 The casting treatment includes a wet casting method in which an undried wet coated layer is pressed against a mirror-polished heated finishing face; a rewetting casting method in which a dried coated layer is again wetted to plasticize it and is pressed against a mirror-polished heated finishing face; and a gel casting method in which a wet coated layer is brought into a gelled state and is pressed against a mirror-polished heated finishing face. The casting methods are most suitable for gloss finish, but other methods may be employed.

20 Fig. 5 shows an example of a post card employing the recording medium thus prepared of the present invention. Fig. 6 shows the cross-section of the post card.

In Fig. 6, the recording medium is constituted of an ink-receiving layer A, a base paper B, and a layer C containing a cationic substance. For example, an image is formed on the face of the layer A by color ink-jet recording, and an address is written on the face of the layer C. The border lines for the post code and the postage stamp may be printed by ink-jet recording or offset printing.

The ink used in the present invention is described below.

The ink comprises a water-soluble dye having an anionic group, water, and a water-soluble organic solvent, and, if necessary, an additive such as a viscosity controlling agent, a pH-controlling agent, an antiseptic agent, a surfactant, an antioxidant, or the like.

30 The water-soluble dye having an anionic group used in the present invention may be selected from the water-soluble dyes of acid dyes, direct dyes, and reactive dyes listed in Color Index without any limitation. Further, any dye having an anionic group such as a sulfonic group and a carboxylic group may be used without limitation even though it is not listed in Color Index. The water-soluble dye herein includes naturally those having a pH-dependent solubility.

35 The water-soluble organic solvent for the ink includes amides such as dimethyl formamide and dimethylacetamide; ketones such as acetone; ethers such as tetrahydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; glycols such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexanetriol, thiodiglycol, hexylene glycol, and diethylene glycol; lower alkyl ethers of polyhydric alcohols such as ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, and triethylene glycol monomethyl ether, monohydric alcohols such as ethanol, isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol; and glycerin, N-methyl-2-pyrrolidone, 1,3-dimethylimidazolidinone, triethanolamine, sulfolane, dimethylsulfoxide, and the like. The content of the above water-soluble organic solvent in the ink is preferably in the range of from 1% to 50% by weight, more preferably from 2% to 30% by weight, but is not limited thereto.

40 The ink may contain, if necessary, other additives such as a viscosity-adjusting agent, a pH-controlling agent, an antiseptic agent, a surfactant, an antioxidant, an evaporation accelerator, and the like. The selection of the surfactant is particularly important for controlling the penetration of the liquid.

The ink has preferably the following properties at around 25°C: a pH of from 3 to 12, a surface tension of from 10 to 60 dyn/cm, and a viscosity of from 1 to 30 cp. More preferably, the surface tension of the respective color inks of yellow, magenta, and cyan is in the range of from 25 to 40 dyn/cm in view of rapid ink absorption and of clear image formation without ink running.

50 For achieving the effects of the present invention more effectively, the ink may contain, in addition to the above mentioned components, an anionic surfactant, or an anionic high-molecular substance, or the aforementioned amphoteric surfactant adjusted to a pH above the isoelectric point. Any usual anionic surfactant including carboxylate salt type surfactants, sulfate ester type surfactants, sulfonate acid type surfactants, and phosphate ester type surfactant may be used without disadvantages. The useful anionic high-molecular substance includes alkali-soluble resins such as sodium polyacrylate, and copolymers of acrylic acid with another monomer, but is not limited thereto.

55 The ink-jet recording system is explained below.

The image forming method of the present invention is applicable to any known ink-jet recording system which ejects droplets of an ink through a nozzle to apply ink onto the recording medium. A typical example of the effective

ink-jet recording system is disclosed in Japanese Patent Application Laid-Open No. 54-59936, in which thermal energy is given to the ink to cause abrupt change of the volume of the ink and to eject ink from a nozzle by the phase change energy.

An example of the ink-jet recording apparatus which is suitable for ink-jet recording of the present invention is explained by reference to the drawings. Figs. 1, 2, and 3 illustrate examples of the construction of a head which is the essential part of the apparatus.

In these drawings, a head 13 is constructed by bonding a plate of glass, ceramics, plastics, or the like having grooves 14 for ink flow with a heat-generating head 15 for thermal recording. (The heat-generating head is not limited to the one shown in the drawings.) The heat-generating head 15 is constituted of a protection layer 16 formed from silicon oxide or the like; aluminum electrodes 17-1, 17-2; a heat-generating resistance layer 18 made of nichrome or the like; a heat-accumulating layer 19; and a heat-radiating substrate plate 20 made of alumina or the like.

The ink 21 fills an ejection orifice (fine nozzle) 22, and has a meniscus 23 formed by a pressure P.

On application of an electric signal information to the electrodes 17-1, 17-2 of the head, the region denoted by a symbol "n" on the heat-generating head 15 generates heat abruptly to form bubbles in the ink 21 on that region, the pressure of the bubble pushes out the meniscus 23 to eject the ink 21 from the orifice 22 in a shape of droplets 24. The ejected ink droplets travel toward a recording sheet 25.

Fig. 3 shows an external appearance of a multiple head integrating a plurality of heads shown in Fig. 1. The multiple head is formed by bonding a glass plate 27 having multiple grooves 26 with the heat-generating head 28 like the one shown in Fig. 1. Fig. 1 is a sectional view of the head 13 along the ink flow path, and Fig. 2 is a sectional view taken at the line 2-2 in Fig. 1.

Fig. 4 shows an example of the entire of the ink-jet recording apparatus equipped with the above-described head. In Fig. 4, a blade 61 as a wiping member is held at one end of the blade by a blade-holding member, forming a fixed end in a shape of a cantilever. The blade 61 is placed at a position adjacent to the recording region of the recording head, and, in this example, is held so as to protrude into the moving path of the recording head. The cap 62 is placed at a home position adjacent to the blade 61, and is constituted such that it moves in the direction perpendicular to the moving direction of the recording head to come into contact with the ejection nozzle face to cap the nozzle. An ink absorbent 63 is placed at a position adjacent to the blade 61, and is held so as to protrude into the moving path of the recording head in a manner similar to that of the blade 61. The blade 61, the cap 62, and the absorbent 63 constitute an ejection recovery device 64. The blade 61, and the absorbent 63 serve to remove off water, dust, and the like from the face of the ink ejection nozzle.

A recording head 65 has an energy-generating means for the ejection, and conducts recording by ejecting the ink onto a recording medium opposing to the ejection nozzle face. A carriage 66 is provided for supporting and moving the recording head 65. The carriage 66 is engaged slidably with a guide rod 67. A portion of the carriage 66 is connected (not shown in the drawing) to a belt 69 driven by a motor 68, so that the carriage 66 is movable along the guide rod 67 to the recording region of the recording head 65 and the adjacent region thereto.

A paper sheet delivery device 51 for delivery of a recording medium and a paper sheet delivery roller 52 driven by a motor (not shown in the drawing) delivers a recording medium to the position opposing to the ejection nozzle face of the recording head, and the recording medium is delivered with the progress of the recording to a paper discharge device provided with paper sheet-discharging rollers 53.

In the above constitution, when the recording head 65 returns to the home position on completion of recording, the cap 62 of the ejection-recovery device 64 is positioned out of the moving path of the recording head 65, and the blade 61 is allowed to protrude to the moving path. Thereby, the ejecting nozzle face of the recording head 65 is wiped. To cap the ejection face of the recording head 65, the cap 62 protrudes toward the moving path of the recording head to come into contact with the ejection nozzle face.

When the recording head 65 is made to move from the home position to the record-starting position, the cap 62 and the blade 61 are at the same position as in the above-mentioned wiping step, so that the ejection nozzle face of the recording head 65 is wiped also in this movement.

The recording head is moved to the home position not only at the completion of the recording and at the time of ejection recovery, but is also moved at a predetermined intervals during recording from the recording region. The nozzle is wiped by such movement.

For color printing by ink-jet recording, four recording heads holding respectively inks of black, cyan, magenta, and yellow are juxtaposed horizontally or vertically on the carriage 66. The inks may be three colors of cyan, magenta, and yellow in place of the four colors.

The present invention is described below in more detail by reference to examples. The term "parts" in Examples is based on weight unless otherwise mentioned.

Example 1

(Preparation of Recording Paper Base Sheet)

5 A mixture of 80 parts of LBKP and 20 parts of NBKP was beaten to C.S.F of 430 mL for use as the starting pulp. Thereto, were mixed 10 parts of kaolin (produced by Tsuchiya Kaolin K.K.), 0.4 part of cationized starch, 0.2 part of polyacrylamide (produced by Harima Kasei K.K.), and 0.1 part of neutral rosin sizing agent (Size Pine NT, produced by Arakawa Kagaku K.K.). From the mixtures, Recording Paper Base Sheet L of a basis weight of 190 g/m² was prepared in a conventional manner.

10 On one face of this recording paper base sheet, the liquid prepared by mixing and dissolving the components below was impregnated, and dried to prepare Base Paper Sheet A. The amount of impregnation after drying was 2 g/m².

(Impregnation Liquid Composition A)

15 **Polyallylamine** **0.8 part**
(PAA-10C, Nitto Boseki Co., Ltd.)

20 **Water** **99.8 parts**

Coating Liquid X for the ink-receiving layer was prepared which had the composition below. This coating liquid was applied on the other face of Base Paper Sheet A to obtain Recording Paper Sheet 1 of the present invention. The dry coating amount was adjusted to 8.0 g/m².

25 (Coating Liquid X for Ink-Receiving Layer)

30	Fine powdery silica (Mizuka Sil P-78D, Mizusawa Kagaku K.K.)	10 parts
	Polyvinyl alcohol (PVA 117, Kuraray Co., Ltd.)	4 parts
35	Polyallylamine hydrochloride (PAA-HCl-3L, molecular weight: 10,000, Nitto Boseki Co., Ltd.)	0.6 part
	Water	85.4 parts

40 The inks of yellow, magenta, cyan, and black: (1) -Y, (1) -M, (1) -C, and (1) -K were prepared by mixing the components below and filtering them through a membrane filter of a pore size of 0.22 μm (Fluoropore Filter, trade name, Sumitomo Electric Industries, Ltd.) under pressure.

(1) -Y

45 **C.I. Direct Yellow 86** **2 parts**
Thiodiglycol **10 parts**
50 **Urea** **4 parts**
Acetylenol EH **0.1 part**
55 **Water** **balance**

(1) -M

The same as (1) -Y above except that the dye was replaced by 2.5 parts of C.I. Acid Red 35.

(1) -C

The same as (1) -Y above except that the dye was replaced by 2.5 parts of C.I. Direct Blue 199.

(1) -K

The same as (1) -Y above except that the dye was replaced by 3 parts of C.I. Food Black 2.

On the resulting recording paper sheet, a color image was formed with the above-mentioned inks by means of a recording apparatus which was equipped with a bubble jet type recording head having 14 recording nozzles per mm and ejecting ink droplets by action of thermal energy. The recorded image was evaluated as below.

1. Surface Image Quality:

On the surface of the ink-receiving layer of the recording paper sheet, solid images were printed at 100% duty and 200% duty in adjacency to each other. the sharpness at the borders between the respective colors was evaluated visually. The recording paper sheet on which sharp border lines were observed was evaluated as "Good", and the one on which the border lines were not sharp was evaluated as "Poor" in surface image quality.

2. Image Density:

On the face of the recording paper sheet reverse to the ink-receiving layer, a solid image was printed with the black ink at 100% duty. After left standing for 12 hours, the printed solid image was subjected to measurement of reflection density by means of a reflection densitometer, Macbeth RD-918 (MacBeth Co.).

3. Water-fastness:

Onto the characters printed at 100% duty on the face of the recording paper reverse to the ink-receiving layer, a drop of water was allowed to fall from a dropping pipet, and was dried spontaneously. After drying, the printed characters were evaluated visually. The recording paper sheet on which the images did not run but became fat was evaluated as "Good" in water fastness. The one on which the characters did not run and did not become fat was evaluated as "Excellent". The one on which the characters ran but were decipherable was evaluated as "Fair". The one on which the characters were not decipherable was evaluated as "Poor".

4. Resistance to Percolation of Applied Ink to Front Face during Water-Fastness Test at Reverse Face:

Onto the solid image printed at 100% duty on the face of the recording paper sheet reverse to the ink-receiving layer, a drop of water was allowed to fall from a dropping pipet, and was dried spontaneously. The front face (ink-receiving layer surface) was examined visually. The recording paper sheet on which percolation of the once-dried ink to the front face was obvious was evaluated as "Poor" in resistance to percolation. The one on which the percolation is slight was evaluated as "Fair". The one on which the percolation was not observed at all was evaluated as "Good".

5. Color Development:

The tint of magenta-, and cyan-color printed areas were examined visually. The recording paper on which the color saturation is high and the colors are clear was evaluated as "Good" in color development. The one on which the color saturation is low and the colors are dusky was evaluated as "Fair". The one on which the color saturation is low and the colors are significantly dusky was evaluated as "Poor".

6. Quality of Recorded Characters:

Intricate Chinese characters were printed at 100% duty. The recording paper sheet on which sharp letters were printed was evaluated as "Good" in quality of recorded characters. The one on which the printed letters were not decipherable was evaluated as "Poor". The one on which the printed letters was of low quality but was decipherable was evaluated as "Fair".

Example 2 and Comparative Example 1

Impregnation Liquids B and C having the compositions below were prepared, and the respective liquids were impregnated into the aforementioned Recording Paper Base Sheet L in the same manner as in Example 1 to obtain Base Paper Sheets B and C. The amount of impregnation after drying was adjusted to 2.0 g/m². Thereon, the aforementioned Coating Liquid X was applied in the same manner as in Example 1 to obtain Recording Paper Sheet 2 and Comparative Recording Paper Sheet 1.

(Impregnation Liquid Composition B)

Benzalkonium chloride (G-50, Sanyo Chemical Industries Ltd.)	0.2 part
Polyallylamine (PAA-10C, Nitto Boseki Co., Ltd.)	0.8 part
Water	99.0 parts

(Impregnation Liquid Composition C)

Water only	(Amount of application: 0 g/m ²)
------------	--

Example 3

Recording Paper Base Sheet N of a basis weight of 140 g/m² was prepared in the same manner as Recording Paper Base Sheet L. Impregnation Liquid D of the composition below was prepared, and Base Paper Sheet D was prepared in the same manner as in Example 1. The amount of impregnation after drying was adjusted to 2.0 g/m².

(Impregnation Liquid Composition D)

Benzyltributylammonium chloride (BTBAC, Sanyo Chemical Industries, Ltd.)	0.4 part
Polyallylamine (PPA-10C, Nitto Boseki Co., Ltd.)	0.6 part
Water	99.0 parts

Coating Liquid Y for an ink-receiving layer having the composition below was applied on Base Paper Sheet D by an applicator in a dry solid amount of 10 g/m², and the applied matter was treated with aqueous 10% calcium formate. The coating film, while it was wet, was pressed and dried with a stainless roll heated at 100°C to obtain Recording Paper Sheet 3 of the present invention having mirror gloss.

(Coating Liquid Y for Ink-Receiving Layer)

Fine powdery silica (Mizuka Sil P-78D, Mizusawa Kagaku K.K.)	6 parts
Polyvinyl alcohol (PVA 117, Kuraray Co., Ltd.)	1 parts
Styrene-butadiene latex	1 part

Continuation of the Table on the next page

(continued)

(Sumitomo Naugatuck K.K.)	
Polyallylamine hydrochloride	0.6 part
(PAA-HCl-3L, molecular weight: 10,000, Nitto Boseki Co., Ltd.)	
Water	91.4 parts

Example 4

Impregnation Liquid E having the composition below was prepared, and was impregnated into Recording Base Paper Sheet L to obtain Base Paper Sheet E. The amount of impregnation after drying was adjusted to 0.5 g/m².

Thereon, the above Coating Liquid X was applied in the same manner as in Example 1 to obtain Recording Paper Sheet 4 of the present invention. The amount of dry coating was adjusted to 8.0 g/m².

(Impregnation Liquid Composition E)

Aluminium basic lactate	0.1 part
(Takiseram G-17P, Taki Chemical Co., Ltd.)	
Polyallylamine hydrochloride	0.9 part
(PAA-HCl-3L, molecular weight: 10,000, Nitto Boseki Co., Ltd.)	
Water	99.0 parts

Example 5

Impregnation Liquid F having the composition below was prepared, and was impregnated into Recording Base Paper Sheet L in the same manner as in Example 1 to obtain Base Paper Sheet F. The amount of impregnation after drying was adjusted to 0.5 g/m².

Thereon, Coating Liquid Z for an ink receiving layer having the composition below was prepared, and was applied in the same manner as in Example 1 to obtain Recording Paper Sheet 5 of the present invention. The amount of dry coating was adjusted to 8.0 g/m².

(Impregnation Liquid Composition F)

Basic polyaluminium hydroxide	0.2 part
(Paho#2S, Asada Kagaka K.K.)	
Polyallylamine hydrochloride	0.8 part
(PAA-HCl-3L, molecular weight: 10,000, Nitto Boseki Co., Ltd.)	
Water	99.0 parts

(Coating Liquid Z for Ink-Receiving Layer)

The fine powdery silica in Coating Liquid X for ink-receiving layer was replaced by fine powdery alumina (trade name: AKP-G015, Sumitomo Chemical Co., Ltd.).

Example 6

Recording Paper Sheet 6 of the present invention was prepared in the same manner as in Example 3 except that Impregnation Liquid G having the composition below was impregnated into the aforementioned Recording Paper Base Sheet N in an amount of dry solid coating of 0.5 g/m².

(Impregnation Liquid Composition G)

Aluminium acrylate (P-3, Asada Kagaku K.K.)	0.2 part
Polyallylamine hydrochloride (PAA-HCl-3L, molecular weight: 10,000, Nitto Boseki Co., Ltd.)	0.8 part
Water	99.0 parts

Example 7

Recording Paper Base Sheet M having a basis weight of 60 g/m² was prepared in the same manner as Recording Paper Base Sheet L. Impregnation Liquid H shown below was impregnated thereto in the same manner as in Example 1 to obtain Base Paper Sheet H. The dry coating amount was adjusted to 0.5 g/m². Thereon Coating Liquid X for an ink-receiving layer was applied in the same manner as in Example 1 to obtain Recording Paper Sheet 7 of the present invention.

(Impregnation Liquid Composition H)

Polyallylamine hydrochloride (PAA-HCl-3L, molecular weight: 10,000, Nitto Boseki Co., Ltd.)	0.4 part
Water	99.6 parts

Example 8

The aforementioned Coating Liquid X for an ink-receiving layer was applied on the aforementioned Recording Paper Base Sheet M in a dry coating amount of 8.0 g/m². Then the aforementioned Impregnation Liquid H was impregnated into the face of the recording paper base sheet reverse to the ink-receiving layer in a dry coating amount of 0.5 g/m² to obtain Recording Paper Sheet 8 of the present invention.

Example 9

Recording Paper Sheet 9 was prepared in the same manner as in Example 7 except that the dry coating amount of Impregnation Liquid H was changed to 2.0 g/m².
The results of Examples and Comparative Example are summarized in Table 1.

Table 1 : Evaluation Results of Examples 1-9 and Comparative Example 1

Example	Impreg- nation liquid for base paper sheet	Impreg- nation to base paper sheet (g/m ²)	Basis weight of recording paper sheet (g/m ²)	Image quality on front face	Image density on reverse face	Water fastness on reverse face	Perco- lation to front face	color develop- ment on reverse face	Character quality on reverse face
1	A	2	200	Good	1.16	Good	Good	Good	Good
2	B	2	200	Good	1.23	Excellent	Good	Good	Good
3	D	2	150	Good	1.25	Excellent	Good	Good	Good
4	E	0.5	200	Good	1.07	Excellent	Good	Fair	Fair
5	F	0.5	200	Good	1.08	Excellent	Good	Fair	Fair
6	G	0.5	150	Good	1.07	Excellent	Good	Fair	Good
7	H	0.5	70	Good	1.06	Fair	Fair	Fair	Fair
8	H	0.5	70	Good	1.06	Fair	Fair	Fair	Fair
9	H	2	70	Good	1.12	Good	Fair	Fair	Fair
<u>Comparative Example</u>									
1	C	0	200	Good	0.95	Poor	Good	Good	Poor

As shown in the above Examples and Comparative Examples, the recording medium of the present invention is

capable of forming sharp color images on the one face thereof with high density and high resolution by ink-jet recording, and is also capable of forming images on the reverse face, on which no ink-receiving layer is provided, by ink-jet recording with high quality and water-fastness of the recorded images. On the reverse face, writing can be practiced similarly as on plain paper because of absence of an ink-receiving layer. Therefore, the recording medium of the present invention is suitable for post cards and other cards. The recording mediums of Examples 1 to 9 with a cationic substance applied on the reverse face gave high water fastness of the recorded image, whereas the recording medium of Comparative Example 1 without a cationic substance gave low water fastness of the recorded image. The recording mediums of Examples 2 to 6, where a low-molecular cationic substance of molecular weight of 1000 or lower was used in combination with a high molecular cationic substance, improved the water fastness of the recorded image in comparison with the recording mediums of Examples 1, 7, 8, 9 where a high-molecular cationic substance singly was used.

The recording paper sheets having a larger basis weight of Examples 1 to 6 did not cause percolation of re-dissolved ink to the reverse face even when water drops were deposited for hours.

As explained above, in color ink-jet recording, the recording medium of the present invention makes possible formation of original color images on a post cards or the like cards easily at a low cost.

A recording medium is provided which has an ink-receiving layer mainly composed of an inorganic pigment and a binder on one face of an ink-absorbent base sheet, and a cationic substance applied on, or impregnated into, the reverse face of the base sheet.

Claims

1. A recording medium having an ink-receiving layer mainly composed of an inorganic pigment and a binder on one face of an ink-absorbent base sheet, and a cationic substance applied or impregnated onto or into the other face of the base sheet.
2. The recording medium according to claim 1, wherein the recording medium has a basis weight ranging from 120 g/m² to 200 g/m².
3. The recording medium according to claim 1, wherein a first low-molecular cationic substance having a weight-average molecular weight of not higher than 1000, and a second high-molecular cationic substance having a weight-average molecular weight of not lower than 2000 are applied or impregnated on or into the other face of the base sheet.
4. The recording medium according to claim 3, wherein the first low-molecular cationic substance, and a second high-molecular cationic substance are contained at a weight ratio of from 20/1 to 1/20.
5. The recording medium according to claim 1, wherein the surface of the ink-receiving layer is treated for gloss.
6. The recording medium according to claim 1, wherein the cationic substance is applied or impregnated in an amount ranging from 0.05 g/m² to 7 g/m².
7. The recording medium according to claim 6, wherein the cationic substance is applied or impregnated in an amount ranging from 0.3 g/m² to 3 g/m².
8. An image-forming method comprising applying an ink containing at least a water-soluble dye having an anionic group onto the recording medium as set forth in claims 1 to 7.
9. The image-forming method according to claim 8, wherein the ink is applied to the recording medium by ejecting the ink as liquid droplets from an orifice in accordance with recording signals.
10. The image-forming method according to claim 8, wherein the ink includes four colors of inks of yellow, cyan, magenta, and black.
11. The image-forming method according to claim 8, wherein the ink is applied onto the recording medium by an ink-jet recording system.
12. The image-forming method according to claim 11, wherein the ink-jet recording system is of a type which ejects ink by action of thermal energy to the ink.

FIG. 1

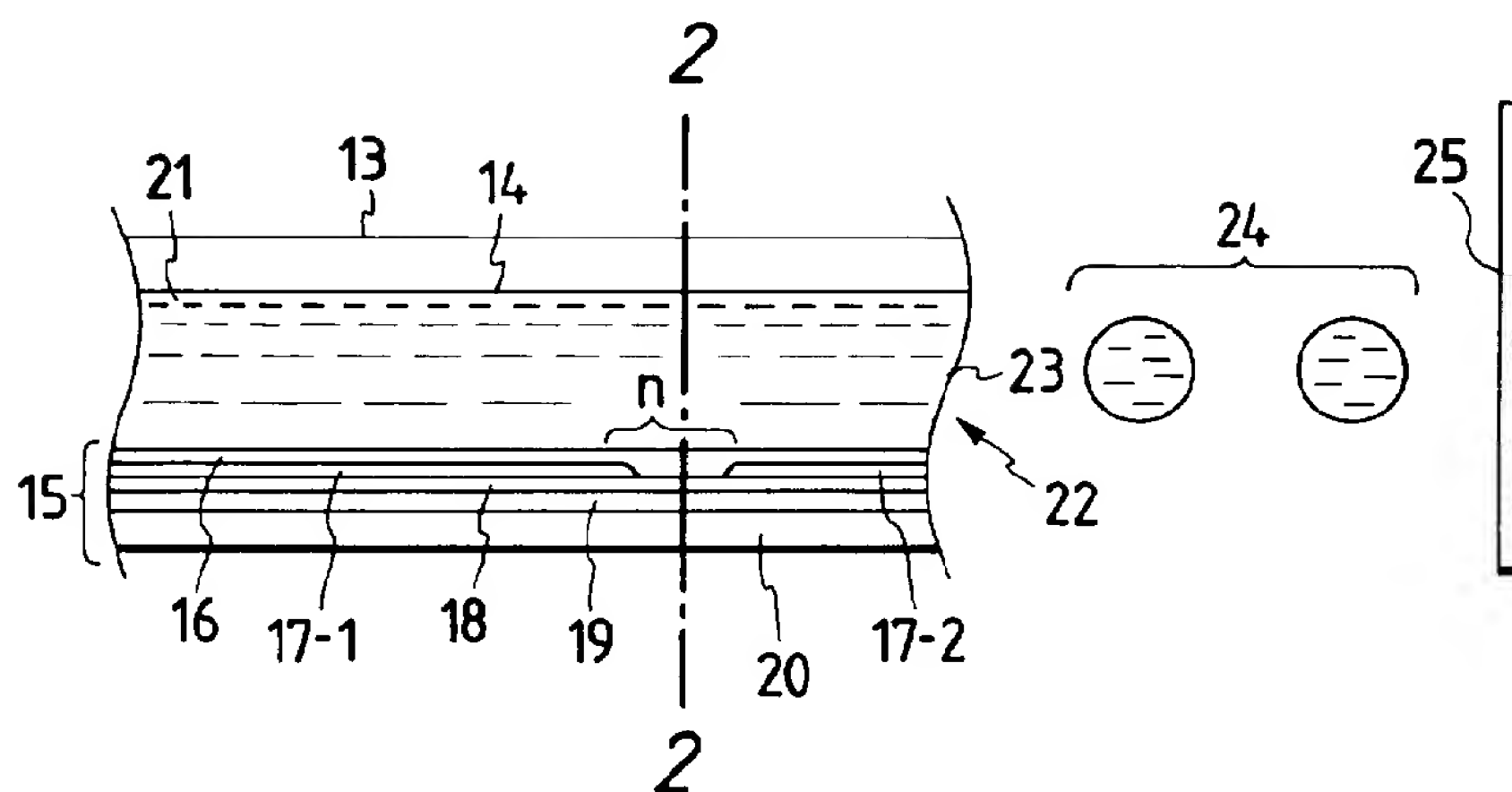


FIG. 2

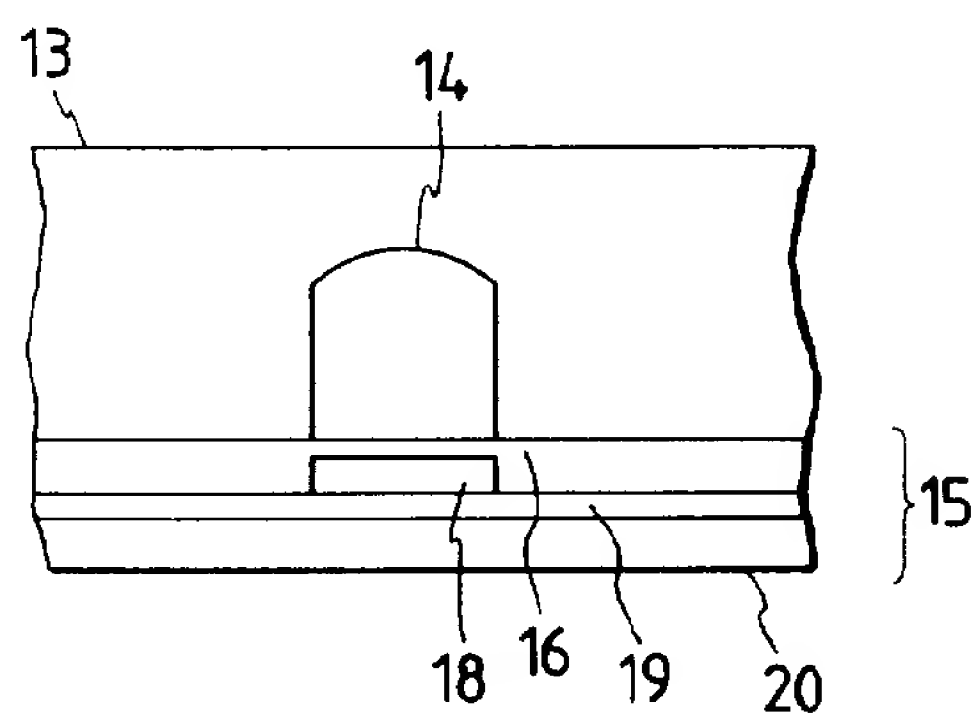
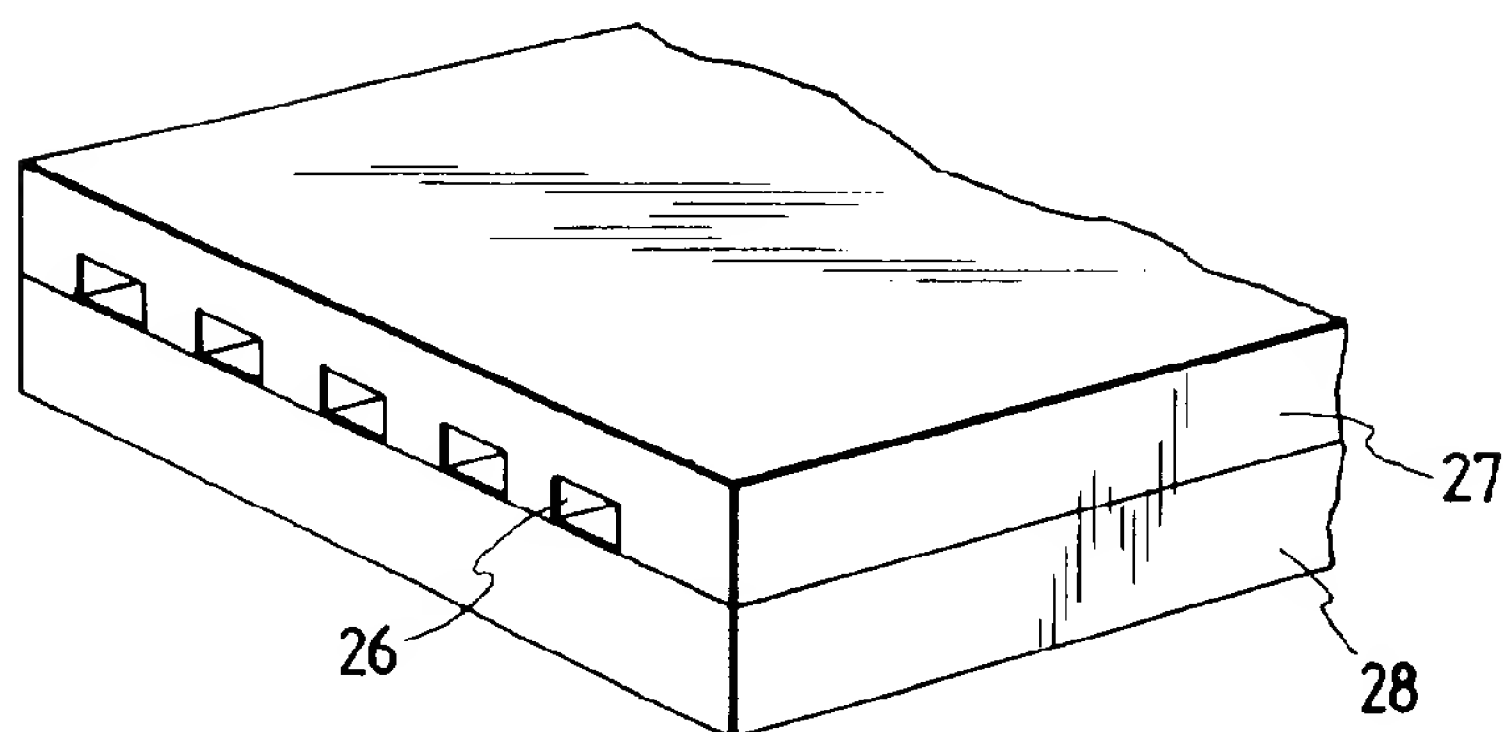


FIG. 3



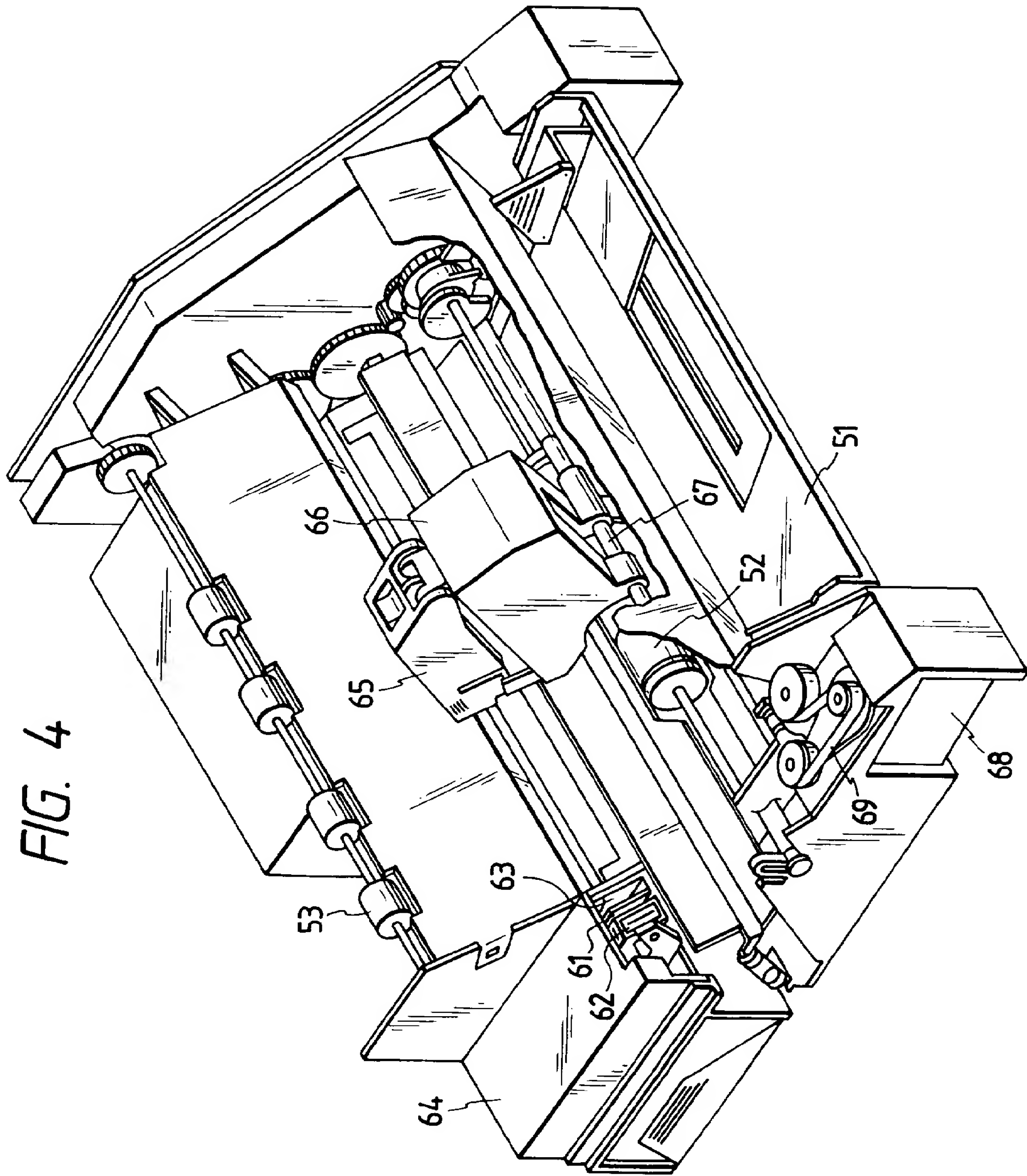


FIG. 5

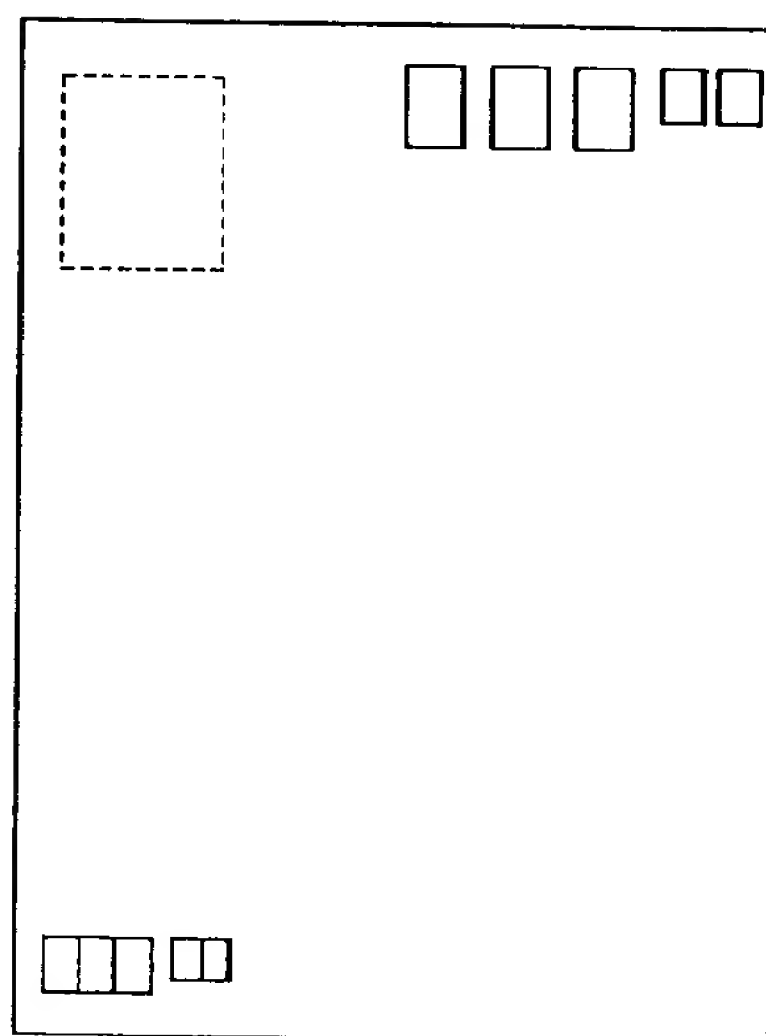
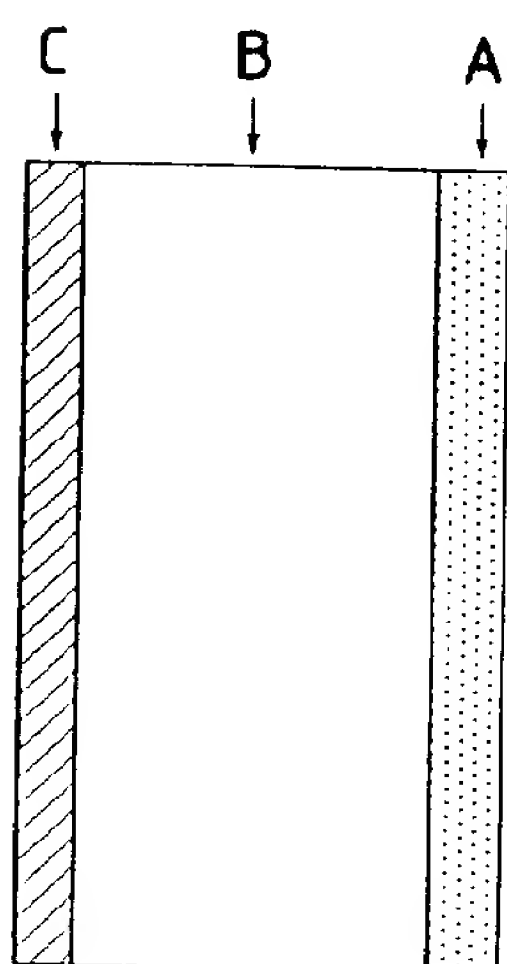


FIG. 6





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 6881

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE-A-43 07 241 (STEINBEIS TEMMING PAPER GMBH & CO) * column 1, line 1 - line 10 * * column 3, line 28 - line 54 * * column 4, line 45 - column 5, line 53 * * claims 1,2,5,8,9,12 * ---	1-12	B41M1/36 D21H19/84
X	EP-A-0 387 893 (JUJO PAPER COMPANY LIMITED) * page 3, line 9 - line 31 * * page 5, line 2 - line 19 * * figures 1-4; examples 1-4 * * claim 1 * ---	1-12	
X	FR-A-2 257 738 (REFLEX PAPIER FABRIK FELIX HEINR. SCHOELLER) * page 3, line 1 - line 23; figure 1 * * claims 1,9; examples 1-3 * ---	1-12	
X	EP-A-0 600 245 (MITSUBISHI PAPER MILLS, LIMITED) * page 5, line 19 - line 40 * * page 6, line 4 - line 15 * * page 6, line 32 - line 35 * * claims 2,3; examples 1-13; table 1 * ---	1-12	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B41M D21H
X	EP-A-0 495 430 (CANON K.K.) * page 3, line 40 - line 44 * * page 5, line 1 - line 36 * * claims 1,8,14,20; examples 1,2 * -----	1-12	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 January 1996	Examiner Bacon, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)